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Contaminated smoke: a simulation of the heavy metal containing aerosols from fires in plutonium glove boxes

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SUMMARY

With the aim of studying the dispersion of plutonium bearing aerosols during glove box fires on a full-size laboratory scale, a special fire-chamber simulating a plutonium handling facility and equipped with the necessary analytical instrumentation was developed.

For comparative fire studies, a 0.6 MW fire source was standardized, with a reproducibility better than 10 %. PMMA (a major glove box construction material) was used as combustible material for this standard fire, to which, if required, samples of other construction materials can be added.

Using cerium-europium oxide as a substitute for plutonium oxide for surface contamination of the material, the percentages of the airborne contamination carried away with the combustion gases and remaining inside the fire chamber after a standard fire, are measured. During the fire, between 60 and 75 % of the original contaminant lanthanide oxide becomes airborne, 1 - 2 % are carried away with the combustion gases into the ventilation outlet.

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1. INTRODUCTION

Plutonium, when used in facilities for fabrication of nuclear fuels, is normally handled only in glove boxes or similar types of containment. The insides of these glove boxes and the equipment they contain become strongly contaminated with plutonium, mostly in the form of plutonium oxide.

For the safety analysis of such a facility, an important question is the spread of plutonium in case of a fire. Then the bulk of the plutonium, involved in the fabrication process, and the contaminant plutonium both contribute to a possible spread of contamination.

For the safety analysis, not only the quantity of plutonium set free inside and outside the buildings is an important factor, but also the particle size distribution of the plutonium containing aerosols, since this determines the distance to which the plutonium is carried, the place where it is deposited, the risk associated with inhalation.

Extensive research has been done on fires in nuclear facilities for hazard evaluation in terms of heat and mass release and their consequences for the ventilation and air-filtering systems ^{1,2,3}. Moreover, small scale burn experiments, involving a few grams of combustible material, have provided data for modelling the source term from contaminated glove box materials, e.g. for the FIRIN compartment code ^{4,5}. However, a code supported only by small-scale fires, is not necessarily valid when applied to scenarios involving for example a whole glove box, i.e. a difference in scale greater than 1000.

Thus large-scale fires in realistic laboratory conditions, in the 0.1 to 1 MW range and involving several kilograms of glove box materials, are still required for safety analyses.

Based upon these considerations, a project to investigate the source term and other consequences of a fire in a fabrication facility for plutonium containing fuels was started at the European Institute for Transuranium Elements.

Since radiation protection considerations preclude large scale fires with plutonium contaminated objects, the project was divided up into two parts :

- study of large scale fires using cerium as a stand-in for plutonium
- study of small scale fires inside glove-boxes using both cerium and plutonium as contaminants.

The results of the former should give input data for modeling studies of real fires.

The results of the latter should give information on combustion and release mechanisms and show up possible differences in behaviour between plutonium and cerium.

The combined results of both studies should give information on effects of scale.

The present report describes the first part of the study of large scale fires. It deals extensively with the technical equipment of the Karlsruhe fire chamber, the supporting analytical methods and instrumentation, and the development of the procedure for the standard polymethylmethacrylate fire. Subsequent reports will describe experiments with other materials exposed to fires and further applications of particle size analysis techniques.

Selection of procedures

Polymethylmethacrylate (PMMA) is a widely used material for the construction and equipment of glove boxes. Since PMMA ignites readily and then burns to completion, it was decided to start the project by establishing a standard PMMA-fire with more or less reproducible characteristics.

Contaminated specimens of the other materials (both combustible or non-combustible), used in or on glove boxes, will then be burned in or exposed to the flames of the standard PMMA fire. The choice of cerium as a stand-in for plutonium was based on the similarity of their chemical properties. Actually, the cerium was mixed with europium, with which it is miscible in most solid compounds, in an atom-ratio $Ce/Eu = 84/16$. The addition of europium lowers the limit of detection of the contaminant and also provides a stand-in for americium, a small amount of which is usually found in plutonium (decay of Pu-241 to Am-241).

Various experimental procedures, especially those that serve to minimize the carry-over of contamination from one fire to the next and certain sampling procedures, were developed gradually as the study progressed.

2. EXPERIMENTAL

2.1 The Fire Chamber

The fire chamber is fast 2/3 the size of a "hot laboratory" at the JRC-Karlsruhe, within which plutonium and similar alpha-emitting elements are handled in about 10 to 15 glove boxes. Figure 1 shows a drawing of the fire chamber, a

rectangular concrete-walled room with a total available volume amounting to 171 m³ (10.3 m length, 3.6 m width and 4.95 m height). The floor is coated with epoxy paint, while the concrete surfaces of walls and ceiling remain rough.

The floor and some parts of the walls are covered, before each experiment, with a layer of strippable paint (GLASURIT, an aqueous dispersion of polymer) in order to collect the settling airborne material.

According to the same principle as in a hot laboratory, the fire chamber is provided with a ventilation system, which forces the air diagonally downward through the room, from a longitudinal duct of 8.70 m length (with a total surface of injection of 0.17 m²) hanging parallel to the ceiling, to another longitudinal duct of 5.50 m length, placed on the floor. The latter is surmounted with a vertical exit channel whose top, at a height of 4.10 m above the floor, passes through the wall towards a ventilator outside the building. The air outlet duct has five vertical orifices which are masked by slightly larger plates, which act as a screen providing a baffle pathway. The total evacuation surface at these screened orifices amounts to 0.56 m².

The ventilation rate can be adjusted between 250 and 3500 m³ h⁻¹, and is regulated (valves) and measured (anemometer) in the air inlet system. The pressure inside the fire chamber is permanently regulated, by a by-pass setting placed in the air outlet system, at -0.4 mbar with respect to the outside, i.e. the same pressure as maintained in a plutonium laboratory at the JRC-Karlsruhe.

In winter, the injected air is automatically pre-heated to 15°C. For drying of the room, this pre-heating can be regulated up to 30 - 40 °C.

2.2. The Fuel Stack

PMMA softens at about 100 °C, decomposition begins at 170 °C, self-ignition is at about 450 °C. In burning, PMMA undergoes pyrolysis from the heat of the ignition source or its own heat of combustion ($\Delta H_c = 26\,000 \text{ KJ Kg}^{-1}$), the volatile pyrolysis products (predominantly the monomer) then burn in the gas phase^{6,7}. At a sufficiently high temperature, a PMMA fire propagates readily when the hot, combustible pyrolysis products become mixed with sufficient oxygen and ignite to cause very rapid surface involvement⁶. This quasi flash propagation is confirmed by the Fig. 2 which shows that the rate of weight loss increases exponentially by an order of magnitude in less than two minutes. However, the

geometry of the fuel stack and the air supply strongly influence the course of the fire and its degree of reproducibility.

For instance, for the same initial weight of PMMA and the same ventilation rate, a cubic box-shaped structure, as used in preliminary experiments, gave a maximum rate of pyrolysis of 11 g s^{-1} after a burning time of 9 min, against about 23 g s^{-1} after 5 to 6 min. with the plate-shaped structure described below.

Finally, for a standard fire the fuel stack consists of 5 square plates of PMMA with sides of 0.32 m, thickness of 8 mm and a 60 mm diameter hole in the center of each plate. Total PMMA weight is 4.7 to 5.1 kg, according to small variations in sizes. The average density of PMMA is 1.18 g cm^{-3} .

These plates are stocked in a steel framework, horizontally above each other with a spacing of 100 mm. In order to prevent premature and non-reproducible collapse of this structure during the fire, each plate is supported by parallel steel wires in addition to the elements holding it at the sides. The fuel stack is placed on a stainless steel tray ($0.64 \times 0.64 \text{ m}$), on the balance described under 2.4. Thus the lower PMMA plate is at a height of 0.465 m, the upper plate at a height of 0.905 m above the floor. The whole system, fuel stack and balance, is placed on another, larger, stainless steel tray ($1.50 \times 0.80 \text{ m}$) for floor protection.

Ignition is carried out by burning 60 ml of ethanol in the tray underneath the fuel stack. The axis of the fire is at nearly a third along the length and halfway across the width of the chamber.

It must be pointed out that the holes in the center of the plates act as a chimney and assure a rapid and complete transmission of the heat of combustion, and thus a reproducible flash ignition.

2.3 Heavy-metal oxide applied as contaminant

2.3.1 Preparation

The mixed oxide $\text{Ce}_{0.84}\text{Eu}_{0.16}\text{O}_x$, used as a contaminant, is prepared from europium (III) oxide and ammonium cerium (IV) nitrate (MERCK, pro analyse), the solutions of which, in nitric acid, are mixed so that a Eu/Ce ratio of 0.2 is obtained. The hydroxides are then co-precipitated with ammonia, filtered and calcined at 900°C . The resulting mixed oxide is ground and divided by sieving into two fractions : greater and smaller than $40 \mu\text{m}$.

2.3.2 Analysis

The addition of europium to the cerium is very beneficial to the analysis of the heavy metal, since the limit of detection by neutron activation is considerably lower for europium than for cerium. The effort for its neutron activation analysis is considerably smaller than in the case of cerium. Once it has been established that no fractionation takes place, the amount of europium may serve as an indicator for the mixture.

A determination of europium in solution by neutron activation, with a detection limit of nearly 2 μg , has been put into practice at the JRC-Karlsruhe using a 5 mg Cf-252 source for the neutron irradiation. The isotope $^{152\text{m}}\text{Eu}$ ($t_{1/2} = 9.3\text{h}$) is measured by gamma-spectrometry at the 121.98 KeV peak. This method is convenient for the analysis of heavy metal in the combustion residues, which, beforehand, are brought into solution by wet decomposition in a mixture of H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$.

By contrast, the neutron activation of europium (and possibly cerium) in quantities ranging from nanogrammes to microgrammes, which is required for the analysis of aerosol sampling filters and deposit samples, needs a much higher neutron flux. This type of analysis, initially carried out in the HFR reactor at the JRC-Petten (The Netherlands, thermal neutron flux: $4.5 \times 10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$), were later performed at the German Center for Cancer Research at Heidelberg, whose lower flux reactor TRIGA II (thermal neutron flux: about $2 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$) allows faster "cooling" after the irradiation of highly concentrated samples. The detection limit for europium varies between 4 and 20 ng depending on the sample support, for an irradiation time of 6 hours and a counting time of 15000 sec.

2.4 Weight Recording

The fuel stack is situated on an electronic balance (Sartorius 5807) with a weighing range of 60 kg, the aim of which is the continuous measurement of the pyrolysis rate by recording the weight of the burning sample.

2.5 Measurements of Temperatures

Temperatures are measured with chromel-alumel thermocouples. A vertical array of 9 thermocouples individually screened from the fire's radiation and regularly spaced at 500 mm is mounted at varying locations in the room. Floor temperature is measured with a thermocouple at 2 mm above the floor and 1.20 m from the axis of the fire, also screened from the fire's radiation. Temperature is also measured at the entrance of the ventilation exit channel and inside it at a height of 2 m above the floor.

2.6 Data Acquisition

Data on temperature distribution and pyrolysis rate are recorded every 30 s by a computer-controlled data logging system (Hewlett-Packard 3497 A). The corresponding time-patterns are automatically drawn using a X-Y-plotter (WATANABE MP 1000) connected to the computer.

2.7 Measurement of Aerosol Concentration

The aerosols (smoke and contamination particles) carried away with the combustion gases, can be sampled on 12 NUCLEPORE filters of 0.8 μm porosity and 50 mm diameter, mounted in the ventilation exit channel at a height of 2.20 m above the floor. These filters can all be independently operated, at any selected time interval during a fire, by means of 12 independently switched rotary pumps at a flow rate of about 40 l min⁻¹. Isokinetic filtration can be assumed by adjusting the inlet nozzle of the filter holders. The weight increase of a NUCLEPORE filter for a given filtration flow rate gives the average smoke concentration in the combustion gases during the corresponding sampling period. The filters are weighed to the nearest 0.1 mg after equilibration with a constant water vapour pressure. The NUCLEPORE filters are subsequently analysed by neutron activation for determination of the europium concentration in the combustion gases.

2.8 Analysis of the Aerosol Particles

When required, special sampling devices for single particle analysis (e.g. grids for electron microscopy) are mounted at the same site as the NUCLEPORE filters.

Close to this site, the combustion products can also be sampled continuously from the exit channel for gas analysis (see 2.9 below) and for aerodynamic particle size measurement.

2.8.1 Aerodynamic Particle Size Measurement

A TSI Aerodynamic Particle Sizer (APS 33) has been used for the particle size analysis of the stock of grounded Ce-Eu-oxide to be used in the experiments. On the other hand, inertial impaction devices have been used for direct measurement of the aerodynamic size of the heavy-metal carrying particles transported with the combustion gases. Initially, the Inertial Spectrometer (INSPEC) developed by V. Prodi et al.¹² for separating aerosol particles according to their aerodynamic diameter was used. In this device, particle separation is achieved by directing the gas and aerosol stream through a sharp 90° bend at a velocity of ~3 m/s into a horizontal channel and through a filter (55 x 20 mm) acting as the bottom of this channel on which the aerosol particles are deposited with decreasing order of inertia. After preliminary calibration using a monodisperse latex aerosol, the assembly was connected to the sampling plug of the vertical exit channel. The deposition sheet was cut into fragments which were analysed for europium.

In further attempts, an ANDERSEN 7-stage cascade impactor was connected to the sampling plug, taking care that the connecting tube was as short as possible. This device was calibrated and operated at a flow of 28.5 l/min. The effective cut-off diameters (ECD) of the successive stages decrease gradually from 10.0 to 0.4 µm. Whatman paper disks (81 mm in diameter), impregnated with glycerine to prevent the particles from bouncing off, were used as the collection surface and subsequently analysed for europium.

2.8.2. Single Particle Analysis

The geometrical diameter, the morphology and the chemical composition of the aerosol particles, transported with the combustion gases, were studied using transmission and scanning electron microscopy combined with microanalytical techniques and automated image processing.

These analyses have been carried out in the Department of Chemistry at the University of Antwerpen (Belgium). In the first experiments, also the feasibility of laser activated mass microprobe analysis (LAMMA) was tested with a view to study not only the distribution and location of heavy metal particulates in

carbonaceous deposits, but also the chemical nature of the smoke and particles that arise from polymers (rubber gloves, PMMA sheets etc.) and whether smoke and particles from polymers are contamination carriers. A Leybold-Heraeus LAMMA-500 probe was employed. Since the use of the laser microprobe is restricted to thin specimens that allow the transmission of the ionising beam, the smoke deposits were collected on EM-grids, and the duration of filtration was limited to 5 sec to avoid overloading of the grids. Theoretically LAMMA has a number of advantages over electron probe microanalysis. These include the capacity to detect all the elements present, the ability to determine organic and inorganic species, a low detection limit (~ 10 ppm for the rare earths), and a high spatial resolution (~ 1 μm). Consequently, the technique is well suited to trace analysis in aerosol particles.

Finally the Electron Probe Micro-Analysis (EPMA) equipped with an energy dispersive Si(Li) detector and automated with the PRC-program (Particle Recognition and Characterization) from Tracor, appeared to be more convenient for morphological and major element characterization of the smoke compounds directly on the Nuclepore filter, and more suitable to identify and size up the Ce-Eu-oxide particles. The electron beam scans a selected area and detects a particle when the intensity of the backscattered electrons exceeds an adjustable threshold and thus indicates a higher Z-value than the substrate. Once a particle is found, maximum, minimum and average diameter are measured, while an X-ray spectrum containing compositional information is accumulated. Then the search for particles is continued. EPMA was performed with a JEOL JXA-733 Superprobe used at an electron energy of 20 KeV and a beam current of ca. 1 nA. At these working conditions a maximum image resolution of 0.05 μm can be obtained. In the initial experiments, the organic material, including the filter, was first eliminated in a low temperature plasma asher (YAMATO-PR 501) and the residue was then transferred onto a grid for SEM. This procedure was very time consuming.

2.9 Analysis of Combustion Gases

The CO and CO₂ contents of the combustion gases were measured by infrared photometry, using a Leyboldt-Heraeus Binos instrument and continuously recorded.

2.10 Measurement of Contaminant Deposition

To estimate the amount of heavy metal deposited on the floor and the walls during the fire, 200 x 200 mm patches of the strippable paint are cut out from 15 to 20 different locations, which may vary for different experiments, then burned to ashes and subsequently analysed by neutron activation (2.3.2).

2.11 Analysis of the Combustion Residues

After pre-calcination, the combustion residue consisting of ash, unburnt fragments of PMMA and part of the contaminant lanthanide oxide, but also of various types of dust (silicate from the concrete, metallic compounds from the framework etc.), was at first analysed by fusion with bisulfate, treatment with hydrofluoric acid and subsequent determination of cerium by coulometry. However, as confirmed later, partial hydrolysis of cerium leads to uncertain results. The present method, wet decomposition in a mixture of sulfuric acid and ammonium sulfate and subsequent neutron activation determination of europium in the solution (section 2.3.2), was calibrated for the residues of PMMA combustion and give reproducible results.

2.12 Description of a fire experiment

The following procedure was adopted for the series of standard contaminated PMMA fires, the results of which are reported in the next chapter.

- a) The floor, the lower steel tray (containing the balance) and parts of the walls pre-selected for deposition sampling are covered with a layer of strippable paint. Then the room is dried at 40-45 °C under the maximum ventilation rate of 3400 m³ h⁻¹ for 15 hours.
- b) Then, and for the following steps, pre-heating of injected air is switched off, with the exception of the automatic pre-heating to 15 °C in winter, and the rate of ventilation is set at 2000 m³ h⁻¹.
- c) A non-contaminated PMMA fire is made, the aim of which is to depose a layer of soot on the ceiling and walls which traps residual heavy metal,

which might have been left over from the preceding experiment. To verify the absence of contamination in the combustion gases, a Nuclepore filter is operated in the exit channel during the whole fire and subsequently analysed by neutron activation.

- d) Then the "real" PMMA fire is carried out. The PMMA is usually contaminated by evenly spreading of Ce-Eu-oxide powder on all five plates, to a surface concentration of 0.1 mg cm^{-2} (i.e. 100 mg per plate). In some experiments only the top plate was contaminated (to 0.5 mg cm^{-2}). It must be pointed out that, at this stage of the study, only the ground fraction of Ce-Eu-oxide powder smaller than $40 \text{ }\mu\text{m}$ in diameter has been used. Data scanning and the first sampling filtration are switched on 60 seconds before the fire is started by igniting a small amount of ethanol. During the fire, the aerosol sampling filters in the exit channel are usually operated one by one with successive filtration times of 2 min during the first 16 min, then with progressively increasing filtration times during the further 30 min. The filtered air volumes are noted. Complete burning of the PMMA fuel stack is achieved after nearly 30 min. Data recording and aerosol sampling are switched off after 45 min. Full ventilation is continued for 15 hours.
- e) Time-dependent parameters deduced from the various collected data are :
- the smoke (predominantly soot) concentration,
 - the heavy metal concentration in the combustion gases carried away by the ventilation,
 - the rate of pyrolysis,
 - the temperature distribution inside the fire chamber. Variation of these parameters for a standard fire is shown in the typical time-patterns of Fig. 2 .
- (f) Deposits are sampled (section 2.10) and combustion residues are collected (section 2.11).
- g) The fire chamber is thoroughly cleaned with a jet of hot water with detergent, left to dry and the rest of the strippable paint is removed.

3. RESULTS AND DISCUSSION

3.1 Characteristics of the Fire and Temperature Distribution

Tab. 1 shows thermal data collected during a number of test fires, using our standardized fuel assembly of 5 plates (as described in chapter 2.4), except for the experiment Nr. 36 which had only one plate. The peak value of the pyrolysis rate always occurred between 280 and 380 s after ignition of the fire.

The parameter P/M (maximal rate of weight loss per initial weight of fuel) is important for the prediction of the material spreading power of a fire. Its mean value from 32 fires, including Nr.36 is $4.7 \text{ g s}^{-1} \text{ kg}^{-1}$ with a standard deviation of 0.3 (relative SD of 6 %). This result shows that our standard fire is reproducible. Further, the continuous gas analysis in the ventilation outlet channel shows that, for a fire involving 4.9 kg of PMMA, the total CO_2 volume calculated from the concentration curve (Fig. 3), i.e. 5.6 m^3 , agrees closely with the value (5.5 m^3) calculated assuming total combustion of the corresponding monomer ($-\text{C}_5\text{O}_2\text{H}_8-$) weight.

In agreement with this, the CO concentration remain below 75 ppm. Thus the combustion of PMMA, under the conditions of the test fires, is practically complete, and the fire power can be calculated from the rate of pyrolysis (monitored with the electronic balance) on the basis of 26 KW for 1 g s^{-1} . Thus the test fires listed in Tab. 1 (except Nr. 36) had a thermal power between 0.55 and 0.65 MW.

Furthermore it has been established that, between 450 and $3000 \text{ m}^3 \text{ h}^{-1}$, variation of ventilation rate does not cause a significant change in the peak combustion rate. This agrees with the fact that, for a maximum rate of pyrolysis of 25 g s^{-1} , assuming stoichiometric combustion of the pyrolysis products, an air supply of $630 \text{ m}^3 \text{ h}^{-1}$ is required for the fire to have sufficient oxygen. Thus the ventilation rate of $2000 \text{ m}^3 \text{ h}^{-1}$, selected for the standard fires, is more than sufficient. It corresponds to 12 air exchanges per hour, i.e. the normal working condition for a hot laboratory at the JRC-Karlsruhe.

The complete temperature distribution in the fire room has been established for each experiment and the corresponding data stored for eventual further modeling. The variation of temperature from the bottom to the top, measured with

the vertical thermocouple array located at 1.70 m from the axis of the fire, shows an almost continuous increase, excepted in the zone between 2 and 3 m height where the temperature remains nearly uniform. The reason for this zone of uniform temperature, which is usually observed, is not yet clear. A simplified profile established with thermocouples spaced at 1 m is shown in Fig. 4.

Some maximum temperatures (mean values of several experiments) reached at the ceiling and in the ventilation exit channel are given in Tab. 2 and clearly show the effect of the downward ventilation system: an increasing rate of ventilation tends to blow down the flames, shielding the ceiling but increasing the temperature in the exit channel. In fact, damage due to overheating was never observed in the fire room. The temperature in the exit channel can reach 80-90°C, whereby the thermal power, carried from the fire chamber, amounts to nearly 52 KW at a ventilation rate of 2000 m³ h⁻¹.

3.2 Smoke Evolution

The evolution of the concentration of the airborne particles carried away in the exit channel is presented, separately for smoke and for heavy metal, in the shape of histograms (see for instance Fig. 2 and 3), since the corresponding data are integrated for each of the successive sampling time intervals.

The rate of generation of smoke does not coincide with the combustion rate, but increases strongly with decreasing fire power. The extracted mass of smoke, in percentage of the initial fuel weight, is quite reproducible. Thus we found, from 17 standard fires, a mean value of 0.61 % with a standard deviation of 0.03. Scanning Electron Microscopy (SEM) of sampling filters showed that most of the smoke deposit consists of chain agglomerates of spherical soot particles with 0.05 to 0.1 µm geometrical diameter (Fig. 5), the usual size for soot from PMMA fires⁸.

3.3 Distribution of Heavy Metals

The overall aim of this work is to describe the spread of heavy-metal particles from a standard contaminated fire. Attention has been focussed on the following points :

- mass inventory (after complete burning) of the cerium, the air-borne part of which having been either carried away by the ventilation or deposited in the fire room, the rest remaining in the ashes,

- mapping of the cerium deposition on floor, walls and ceiling,
- spreading process, particularly nature and size of the particles in which heavy metals are transported, by or together with the smoke.

It was confirmed in early experiments, by neutron activation analysis of both europium and cerium, that the Eu to Ce ratio on the sampling filters does not differ significantly from that of the original contaminant powder. This indicates that no chemical fractionation between the two lanthanides takes place during the transport process. This result justifies the decision to limit all further analyses to the europium determination, the results of which are then converted to values for cerium which is the real plutonium simulant. A considerable number of experiments were necessary to define the many experimental parameters and also to give the first data on the mass balance of heavy metal. During this initial period, the problem of carry over of contamination from one fire-experiment to the next, leading to a distortion of the results, was identified.

3.3.1 Transport into the Ventilation Exit Channel

The main obstacle to a correct inventory was found to be the resuspension of lanthanide oxide deposited on the floor, walls and ceiling, or in the system of outlet ducts, during previous fires, and not completely cleaned away, in spite of thorough in-between cleaning of the room and equipment. The carry-over phenomenon was recognized from the fact that milligram quantities of cerium were still swept along with the combustion gases after a series of 3 non-contaminated fires. Moreover, the concentration of cerium in the ventilation exit channel showed a quite unexpected time-pattern during some of the contaminated fires (Fig. 6 and 7) wherein large quantities of heavy metal were collected in the first minutes after ignition. For instance, in the case of Fig. 6, more than 80 % of the totally collected cerium, in the exit channel, was found during the first 3 minutes. At this time, heating of all but the lowest plate of the fuel stack is still negligible, so that it is very improbable that this transport would be related to the present fire. This transfer from one fire to another leads to an overestimate of the transport of heavy metal from the contaminated burning material (up to 17 % of the original Ce-Eu-oxide in the case of Fig. 7).

In order to minimize the probability of carry-over, a special procedure has been introduced for each experiment, as described above in chapter 2.12. As shown below, application of this procedure greatly reduced the carry-over, and in those

few cases where it still occurred, it could be identified from their anomalous time patterns.

3.3.2 Mass Inventory of Heavy Metal

Data collected in 11 contaminated standard fires are summarized in Tab. 3 (Ventilation rate: $2000 \text{ m}^3 \text{ h}^{-1}$) which gives for the original amount of contaminant (500 mg of $\text{Ce}_{0.84} \text{Eu}_{0.16}\text{O}_x$, i.e. 340 mg of Ce), the percentage transported into the ventilation exit channel and the percentage left in the residue (analysis of the residue failed in Nr. 75). In all these experiments, the original Ce-Eu-oxide powder was sieved to a particle size smaller than $40 \mu\text{m}$. Discontinuities in the numbering correspond to failed experiments or to experiments done under other experimental conditions.

In experiments Nr. 71 and 72, anomalous time patterns revealed a cerium transport in the exit channel of 25 mg and 7 mg respectively before the peak combustion rate occurred. In the remaining nine experiments of Tab. 3, this untimely outflow of heavy metal was not greater than 1 mg (i.e. 0.3 % of the initial contaminant) and their time patterns were all similar to those of Fig. 2. Thus the mean percentage of cerium transported into the exit channel is 1.43 with a standard deviation of 0.47, and the mean percentage of cerium left in the residues is 33 with a S.D. of 6.

In conclusion, apart from a few deviations, which are easy to identify and related to extraneous and typically non-reproducible transfer of contamination from preceding experiments that cannot occur in a single accidental fire, the reproducibility of the heavy-metal mass inventory after a standard experiment is quite high.

3.3.3 Distribution of the Deposition Inside the Room

The above results suggest that the quantity of Ce-Eu-oxide deposited in the fire chamber (total surface : 220 m^2) amounts to between 60 and 70 % of the original contaminant. Thus, from the 340 mg of cerium initially spread onto the PMMA in the case of a standard fire, 200 to 240 mg would be distributed on the floor, walls, ceiling and ducts. An effort was made to verify this assumption experimentally.

The first attempts to sample the actual deposits with repeated smear tests, using a detergent, led to erratic results because of the porosity of the bare or epoxy-

painted concrete. In the further experiments, samples of deposit were collected during the fire by means of test plates of various covering materials attached to the surface at numerous sites inside the chamber. Whatman filter paper impregnated with glycerine and in the shape of disks of 25 cm diameter, subsequently burnt to ash and analysed for europium, gave no satisfactory results: besides the fragility of this material to the high radiant heating during the fire, the surface concentrations of Ce-Eu found on intact disks proved to be an order of magnitude smaller than would be expected from the above calculations. This might be due to thermophoresis effects: during the fire, the concrete floor is significantly colder than the paper sheets attached on it simply by means of an adhesive tape, and the strong thermal gradient pushes the particles away from the hotter surface.

Meanwhile it has been found that the thin layer of strippable paint, applied on the floor to prevent carry-over of contamination from preceding experiments, could also be a suitable sampling sheet for measuring the lanthanide deposition, but only upon sites where the temperature does not exceed 60 - 70 °C, i.e. the whole floor, some lower parts of the walls and, in general, places which are shielded from radiant heat and/or cooled from the outside. For instance, the method is convenient for the wall supporting the gas outlet system, which is a 50 mm thick outer wall. By contrast, on the whole opposite inner wall (300 mm thick) on the air inlet side, the paint patches were overheated and too damaged for subsequent treatment. Numerous deposition measurements have been made by cutting out 200 x 200 mm patches of strippable paint from selected suitable sites, and subsequent analysis for europium. Tab. 4 gives the thus determined values of the surface concentration of cerium at some definite locations, which are marked in Fig. 8, for a series (Nr. 70 to 78) of standard experiments. Moreover, the analysis of the whole paint coating in the lower stainless steel tray (holding the balance) gave, from 3 standard experiments, total deposition values of 3 to 4 mg of cerium, i.e. a surface concentration of nearly 3 mg m⁻² at the foot of the fire.

Although the homogeneity for a given experiment and the reproducibility for a given site are poor, the deposition values shown in Tab. 4, together with those from the lower steel tray, suggest that no more than 3 % of the initial contaminant (that is about 10 mg) have been deposited within a radius of 1.5 m of the fire. Moreover, significantly higher quantities of heavy metal seem to be deposited in the corner adjacent to the vertical gas outlet channel (locations e

and j in Fig. 8), possibly due to a strong impaction of the particles from the diagonally downward ventilation flow.

On the other hand, representative sampling of material deposited on the ceiling and parts of the walls where the temperature exceeds 70°C is much more difficult. Non-combustible sampling materials, such as steel, aluminium, various ceramics and concrete, have been tested in the shape of thin 200 x 200 mm plates. The subsequent treatment consists in washing the lanthanide oxide off in an ultrasonic bath, filtering and determining the europium on the filter. Tab. 5 gives the values of the surface concentration of cerium found on various substrate materials, each of which was tested in a standard fire, whereby 4 identical sampling plates were attached to the ceiling at distances of 0.8 m from the vertical axis of the fuel stack and in directions which were 90° apart (locations a to d).

The results are considerably scattered and suggest differences between the plate materials. These variations could be due to the fact that on the one hand differences in nature of surface influence the degree of adhesion of the particles on the material, and that on the other hand differences in heat conduction and poor contact of the sampling plate with the support might result in a thermophoresis effect, as was already suggested concerning the deposition on Whatman paper.

With the exception of some relatively reproducible results concerning parts of the floor and lower walls, a description of the distribution of the mass of heavy metal deposited on the various sites inside the fire chamber could not be achieved. Moreover, it should be pointed out that in many experiments, non-reproducible "hotspots" containing up to 17 mg m⁻² cerium were found (see for instance in table 4 the location "e" in experiment Nr. 78). This situation, although partly due to sampling problems, is mainly the result of the high degree of turbulence in the atmosphere of the fire chamber during a fire.

4. RELATIONSHIP BETWEEN SMOKE AND HEAVY-METAL AEROSOLS

4.1 Formation of Aerosols in the Fire

In a parallel study of small scale fires, Pickering⁹ described the formation of bubbles at some distance below the surface of melting or burning small pieces of PMMA. These bubbles are presumably filled with pyrolysed products and migrate up the temperature gradient to the surface where they burst, the most efficient temperature for this mechanism being about 200°C. The airborne "primary" carbonaceous particles are then produced by condensation of the pyrolysed products. Their morphology was described by Prodi¹⁰ using a thermophoretic sampling technique on a cold mica sheet coated with carbon, subsequent transfer on a 200 mesh grid and observation by transmission electron microscopy. The primary particles are of compact spherical shape, 0.03 to 0.04 μm in size (count median diameter) and show a log-normal distribution with a geometric standard deviation of 1.25. This suggests that primaries are produced by condensation under relatively uniform conditions. These primaries are of very high concentration, therefore coagulate rapidly to form agglomerates of fluffy or chainlike shape composing the soot, which has a very small aerodynamic diameter and a small mobility.

The initial Ce-Eu-oxide powder, with a particle size smaller than 40 μm , which was used as a contaminant on the fuel plates, has a mass median aerodynamic diameter (MMAD) of 10.5 μm . The distribution, with an apparent geometric standard deviation of around 2.2, (Fig. 9), seems to indicate either 2 superimposed log-normal populations, or a single exponential population as often reported for aerosols originating from fine-grinding processes. The exponential character means in practice that more small particles are present in the contaminant powder than expected from a log-normal distribution of the same MMAD. Moreover, the above features are quite similar to those of aerosols produced in glove boxes for the preparation of mixed uranium-plutonium fuel pellets¹¹, so that this Ce-Eu-oxide powder is also morphologically a suitable simulant for the contaminant in fabrication glove boxes.

Previous measurements showed that the temperature inside the flame of a standard experiment does not exceed 820°C. Results from measurements with an

inertial spectrometer (see section 2.8.1) on small scale fires have shown that under these conditions most of the Ce-Eu oxide mass was carried by particles which were aerodynamically much bigger than the soot¹³. This suggests that the size of the Ce-Eu oxide particles is not greatly affected by the fire and that there is at most a very small interaction between the Ce-Eu oxide and the smoke particles.

4.2 Aerosol Collected in the Ventilation Exit Channel

4.2.1 Aerodynamic Size measurements

The inertial spectrometer (INSPEC) did not yield satisfactory results. This was caused by instabilities in the sampling streams and by the very low aerosol injection flow rate (about 4.2 l/h). Despite continuous sampling during the whole course of the fire, the amounts of heavy metal present on the collecting filter (about 5 ng europium) were close to the detection limit. Nevertheless it could be seen, from 3 experiments, that at least half the mass of heavy metal was present in a white area on the large aerodynamic diameter side of the filter sheet, and thus not associated with the soot particles lying on the low aerodynamic diameter side (black area).

Because of the insufficient sensitivity of the INSPEC instrument, an Andersen cascade impactor was then used in further attempts. With continuous sampling, the total weight of europium distributed on the 7 stages of the impactor normally amounts to less than 2 µg. Two factors contribute to confuse the distribution of the aerodynamic sizes obtained with this device: firstly backgrounds of 40 to 70 ng of europium are found on paper disks impregnated with glycerine, which lead to a high detection limit; secondly the device is designed to operate with the aerosol flowing vertically from top to bottom, and thus a significant loss of particles larger than 10 µm (aerodynamic) occurred in the horizontal aerosol inlet tubing, in spite of attempts to make it shorter and to accelerate the flow.

However, it must be pointed out that the two last stages and the back-up filter of the cascade impactor, corresponding to an effective cut-off diameter smaller than 0.7 µm, collect most of the soot material, whereas at least 70 % of the heavy metal is distributed on the first five stages. This fact confirms the evidence obtained by the INSPEC instrument that the contamination is not carried along by the soot material which has a significantly smaller median aerodynamic diameter.

4.2.2 Morphological and Chemical Analysis

The morphological and chemical analysis of the aerosol particles passing through the ventilation exit channel cannot be made directly on the material collected on the Nuclepore sampling filters used to establish the mass inventory. The filtering time (generally 2 minutes or more), required for an adequate sensitivity in the europium analysis by neutron activation, produces a large excess of carbonaceous smoke particles, which precludes the direct study of the particles containing the Ce-Eu-oxide by scanning electron microscopy (SEM). To overcome this difficulty, the problem was attacked along two lines :

In the first method, the residues of a NUCLEPORE filter, previously calcined in the YAMATO low temperature asher for elimination of the organic material, was transferred to a grid and studied by SEM with simultaneous energy-dispersive X-ray spectrography for determination of the cerium distribution. Results from this procedure are shown in the **Fig. 10 and 11** comparing the original contaminant powder with the particles detected among sampling-filter ashes. The very tedious procedure and repeated breakdowns of the plasma asher allowed us only a few examinations, which however indicated that, firstly, relatively big Ce-Eu-oxide particles are present in the smoke and, secondly, these are very similar, in composition and shape, to the starting material.

The second way to study the oxide particles by SEM, was to reduce drastically the quantity of sampling material in order to study the unchanged particles directly on the filtering support, since this is the only suitable method to demonstrate possible mechanical interactions between carbonaceous and Ce-Eu-oxide particles. The best filtering time is obviously a compromise between the need, on the one hand to discriminate the single soot chains and agglomerates, on the other hand to have a sufficient probability to see a few Ce-Eu-oxide particles. For instance, on the normally used Nuclepore filter through which the combustion aerosol is filtered at a rate of 0.33 m s^{-1} , the surface concentration amounts, in the most favourable case in which single soot chains are still only just distinguishable, to 11 ng cm^{-2} of lanthanide oxide for a sampling time of 5 seconds. This concentration corresponds to about 20 particles of $5 \text{ }\mu\text{m}$ diameter or 2.5 particles of $10 \text{ }\mu\text{m}$ diameter per square centimeter.

In the initial experiments, direct examination of sampling filters was performed with a laser activated mass microprobe analyser LAMMA in addition to SEM. This demonstrated that most of the smoke deposit consisted of soot particles (polycyclic aromatic hydrocarbons) of amorphous nature and cloud-shaped. A typical soot flake is shown in Fig. 12. Crystalline extraneous material was often found associated with these particles (Fig. 13 and 14).

Of the fifty or so soot flakes analysed, only one was found to contain traces of cerium (two low intensity Ce peaks at m/e 140 and 142) dispersed within the soot cloud. Surprisingly no discrete Ce-Eu-oxide particle was found. On the other hand, significant amounts of sodium, potassium, aluminium, titanium, strontium and barium were found in the soot and extraneous material. The experiments thus confirmed that LAMMA can make a contribution to the detailed characterisation of smoke deposits, but that it is more suited to the qualitative or semi-quantitative analysis of low level constituents. Absence of discrete lanthanide oxide particles is statistically inconclusive (5 EM-grids were observed, each of which had an area of 0.1 cm^2), and might be due to possibly unrepresentative sampling conditions.

More suitable than LAMMA to identify and size the Ce-Eu-oxide particles appeared to be electron probe micro-analysis (EPMA) automated with the PRC-programme. Since excess soot present on the filters interferes with the observation of Ce-Eu-oxide particles, the following experimental conditions were chosen: a sampling time of 5 s and a double contamination level (0.2 mg cm^{-2}). Even then, only one experiment yielded usable filters. Fig. 15 shows a detailed view of the deposit contained on an area of 0.03 mm^2 from one of these filters. The large grey amorphous features are soot agglomerates; the small white features are Ce-Eu oxide particles. As is generally observed, the latter do not appear to be fixed to a soot deposit, but occur in the form of discrete particles. This again strongly suggests that they constitute a separate aerosol population. Nevertheless, it is evident from other secondary electron images that many small Ce-Eu-oxide particles are not only surrounded but also partly or totally overlaid by soot agglomerates possibly impacted on these particles during sampling. The size distribution and shape factors of the nearly 200 Ce-Eu-oxide particles identified on a total area of 10.5 mm^2 are shown in Fig. 16 and Fig. 17. The size distribution is presented as a log-normal plot. The geometric standard deviation, σ_g , is 2.2 which falls within the range commonly found for polydispersed aerosols. The fact that the log-normal plot is nearly linear indicates that the aerosol particles belong to one population and, therefore, that the particles were produced

by a single mechanism. The value of the count median diameter (CMD) deduced from Fig. 16 is 1.05 μm ; the value is probably somewhat too high because some small particles overlaid by soot may be undetectable. In the histogram of Fig. 17, the two-dimensional shape factor, which is defined as $SF = (\text{perimeter})^2 / 4 \pi (\text{area})$, is plotted as a function of the number of particles. It can be seen that for 65 % of the Ce-Eu-oxide particles the value of SF lies between 1 and 2; this indicates that they are nearly equiaxial, therefore similar in appearance to those of the original Ce-Eu-oxide powder.

4.2.3 Concluding Remark

The results of the EPMA study thus confirm the evidence presented by the measurements of aerodynamic particle size, that the airborne Ce-Eu-oxide particles are not attached to the carbonaceous agglomerates in the smoke, but that they constitute a distinct aerosol population. The question whether the particles of the contaminant powder remain unchanged in their size during the fire and subsequent transport is not unambiguously solved. In particular, agglomeration or dispersion processes might occur during the fire and the transport. It must be pointed out that a calculation of the median aerodynamic diameters from the observed geometrical sizes (measured by electron microscopy) would give incorrect results for the following reasons :

- Many big particles are clearly agglomerates of low density,
- Many small particles are not detectable,
- Some particles may be plates rather than spheres.

The problem of the aerodynamic size measurement of the contaminated particles carried away by the combustion gases, being essential for safety analyses especially in the respiratory range, will be dealt with again in the second part of this study. For this purpose, a high volume (34 m³ /h) cascade impactor has been purchased.

5. CONCLUSION

From the present first step of this experimental study, the following results were obtained :

- I. In a special chamber, reproducing a typical plutonium-handling facility at the JRC-Karlsruhe, a polymethylmethacrylate (PMMA) fire, equivalent in size to a small glove box, was standardized with the aim of supplying a reproducible fire source for comparative fire studies. Due to well defined experimental conditions (fuel stack structure, ventilation parameters etc.), this standard fire has a reproducibility better than 10 % with regard to the thermal power and the smoke generation.
- II. The standard fuel stack was evenly spread with cerium- europium-oxide powder as a substitute for the actual contaminant plutonium and americium oxides, "contaminant" particle sizes and "contamination" level being similar to those occurring in a typical fuel fabrication glove box. During the fire, between 60 and 75 % of the original contaminant lanthanides becomes airborne, of which about 1 to 2 % are carried away with the combustion gases into the ventilation outlet. The airborne contaminant remaining inside the fire chamber is deposited on the floor, walls and ceiling.
- III. The Ce-Eu oxide particles, carried away with the smoke, are predominantly particles of the contaminant powder, chemically unchanged by the fire, and not attached to soot particles.
The exact degree and nature of the interaction (if there is any) between the soot and the contaminant particles is at present unknown.

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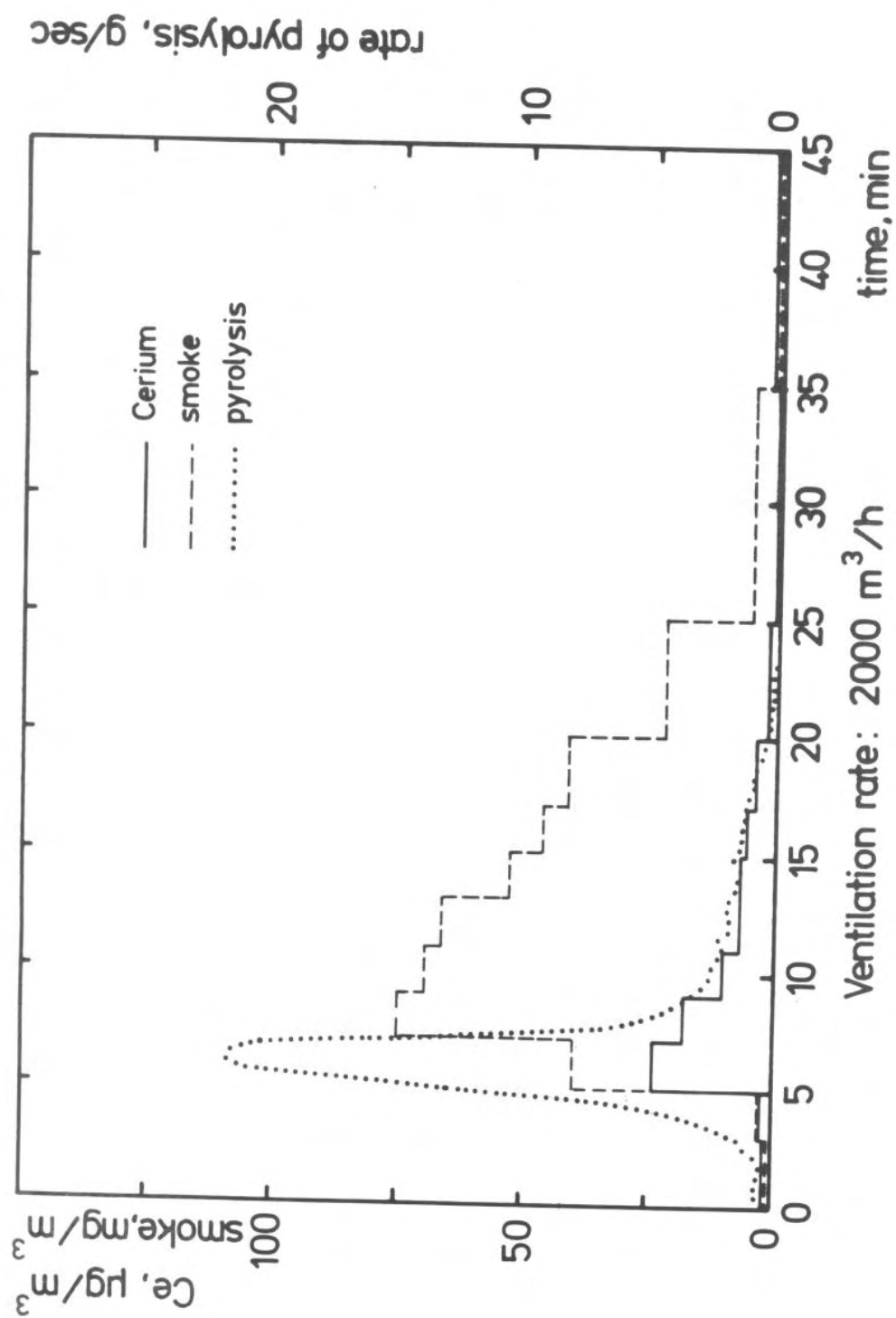


Fig. 2 Time pattern of a standard PMMA fire. The percentage of cerium carried away by the ventilation is 1.9

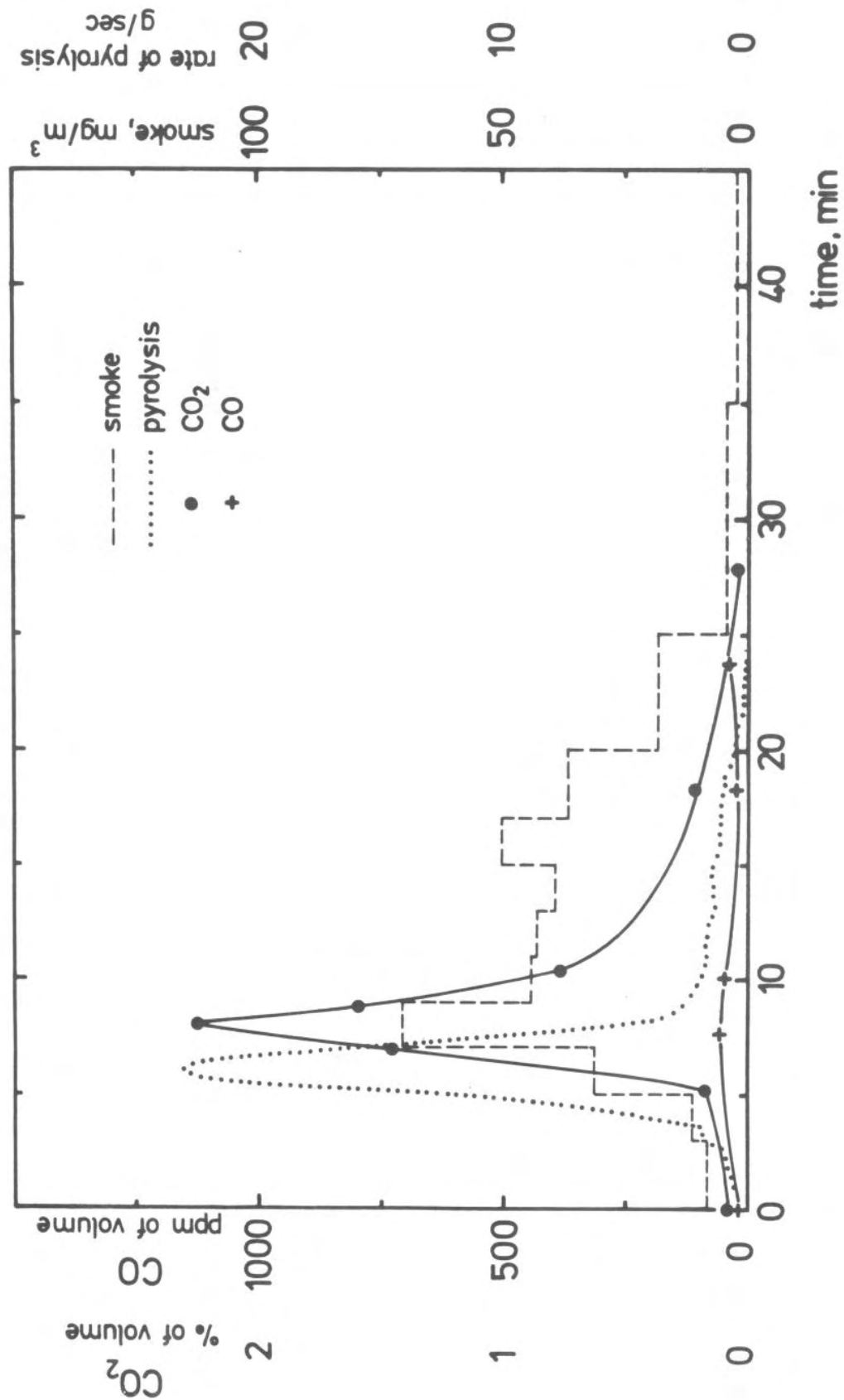


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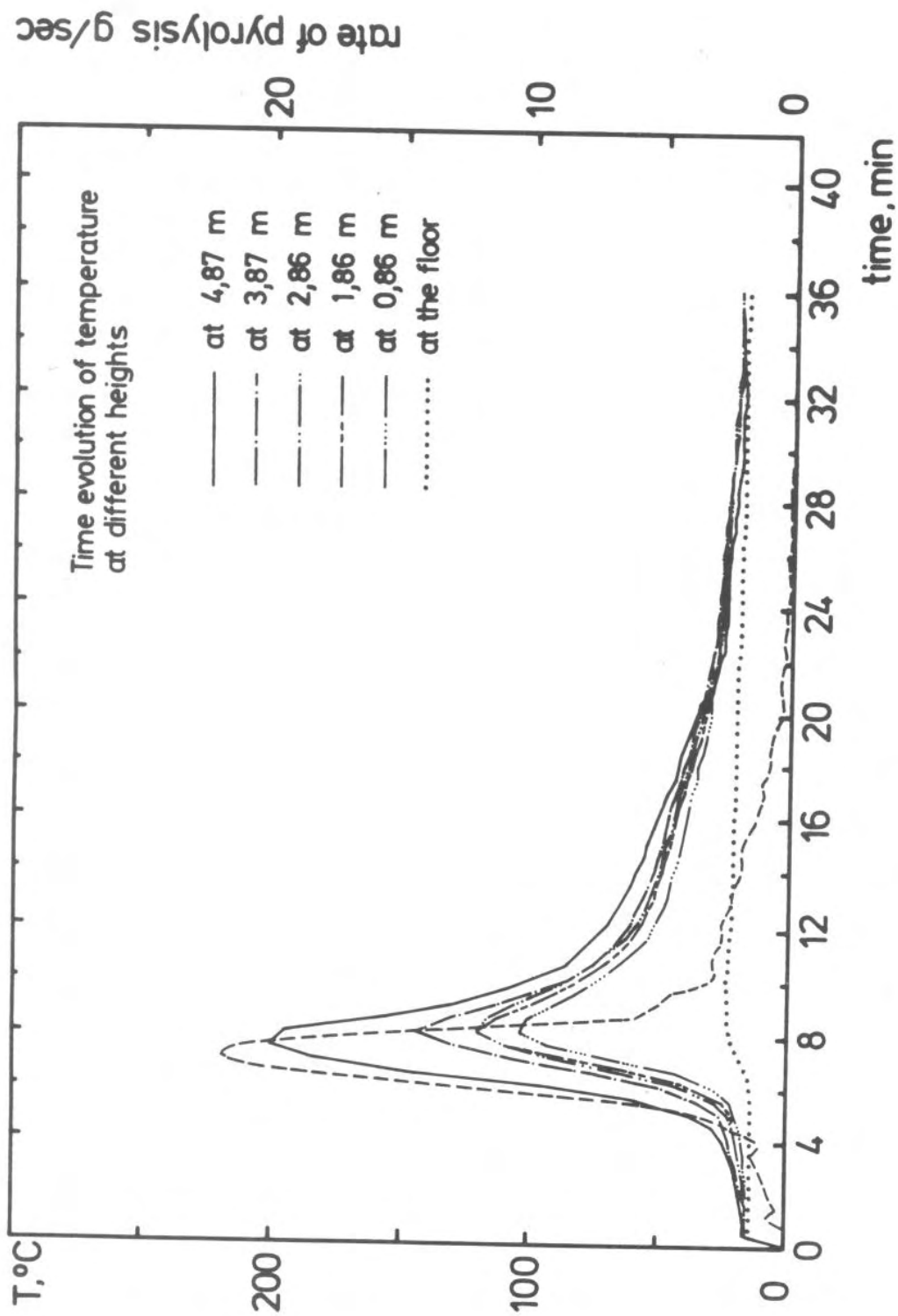


Fig. 4 Temperature profile established with a vertical thermocouple array located at 1.70 m from the axis of a PMMA standard fire. The thermocouples are spaced at 1 m from each other

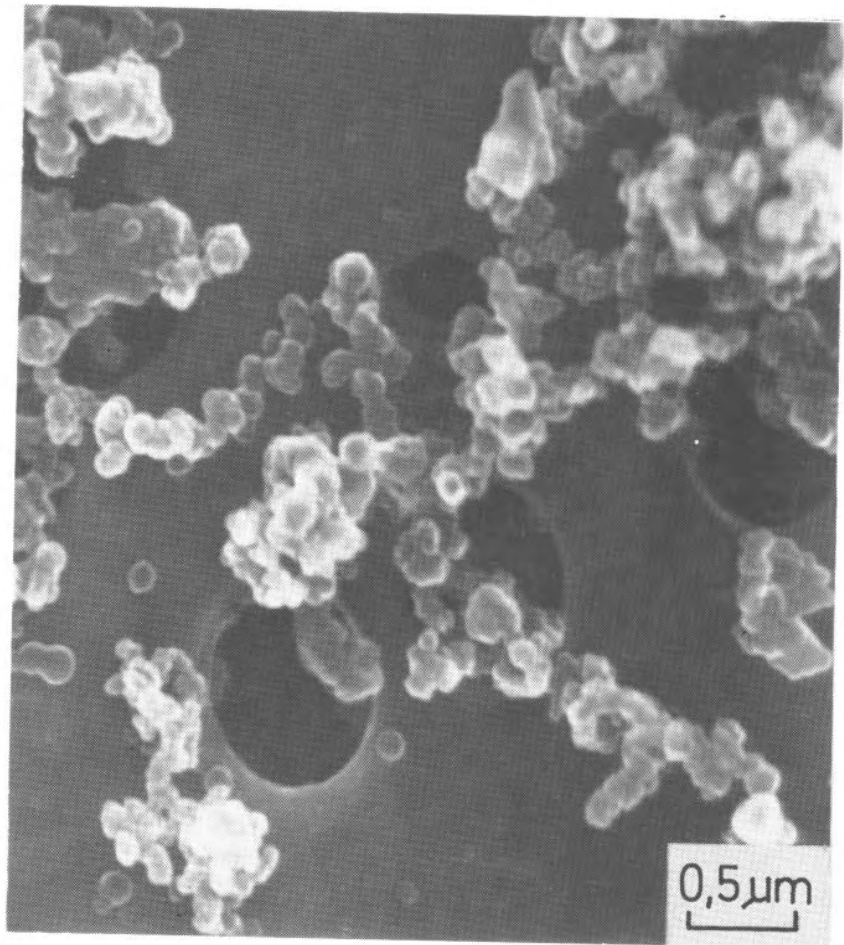


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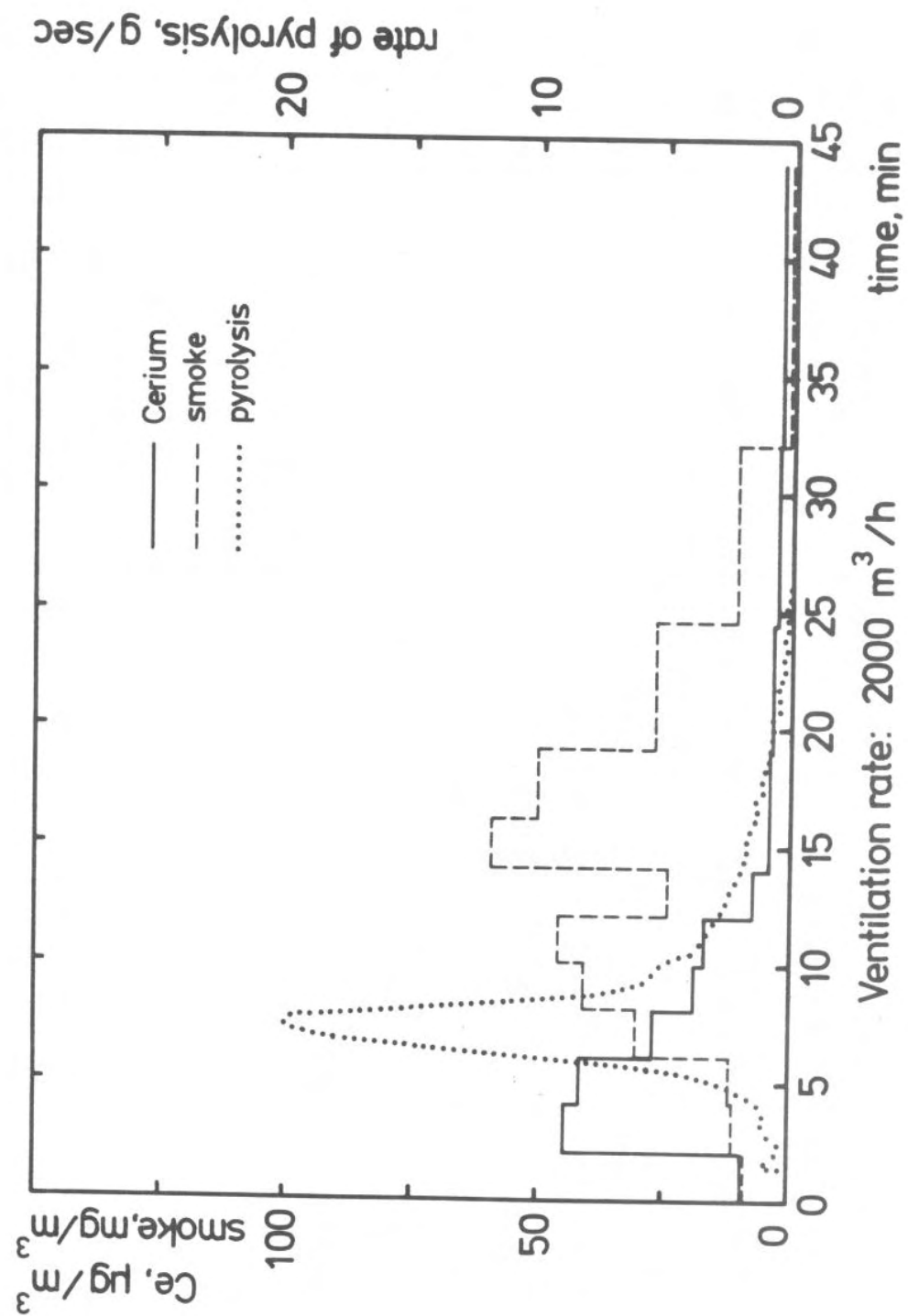


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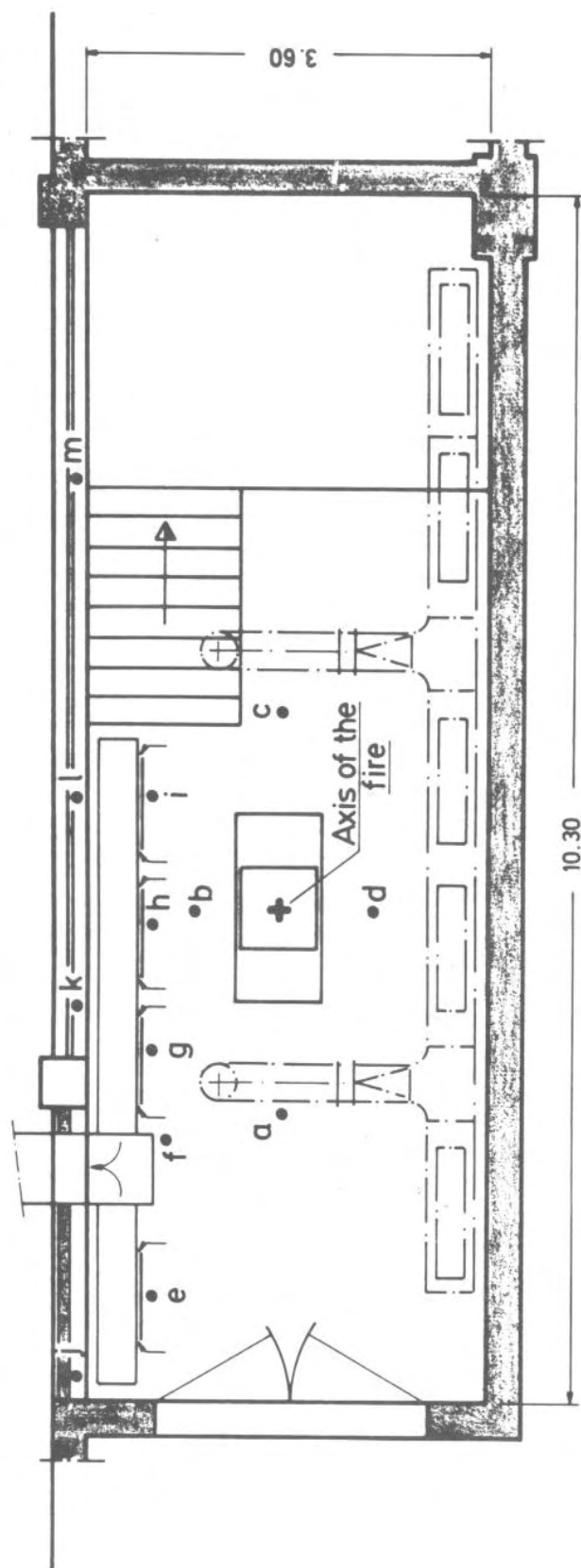


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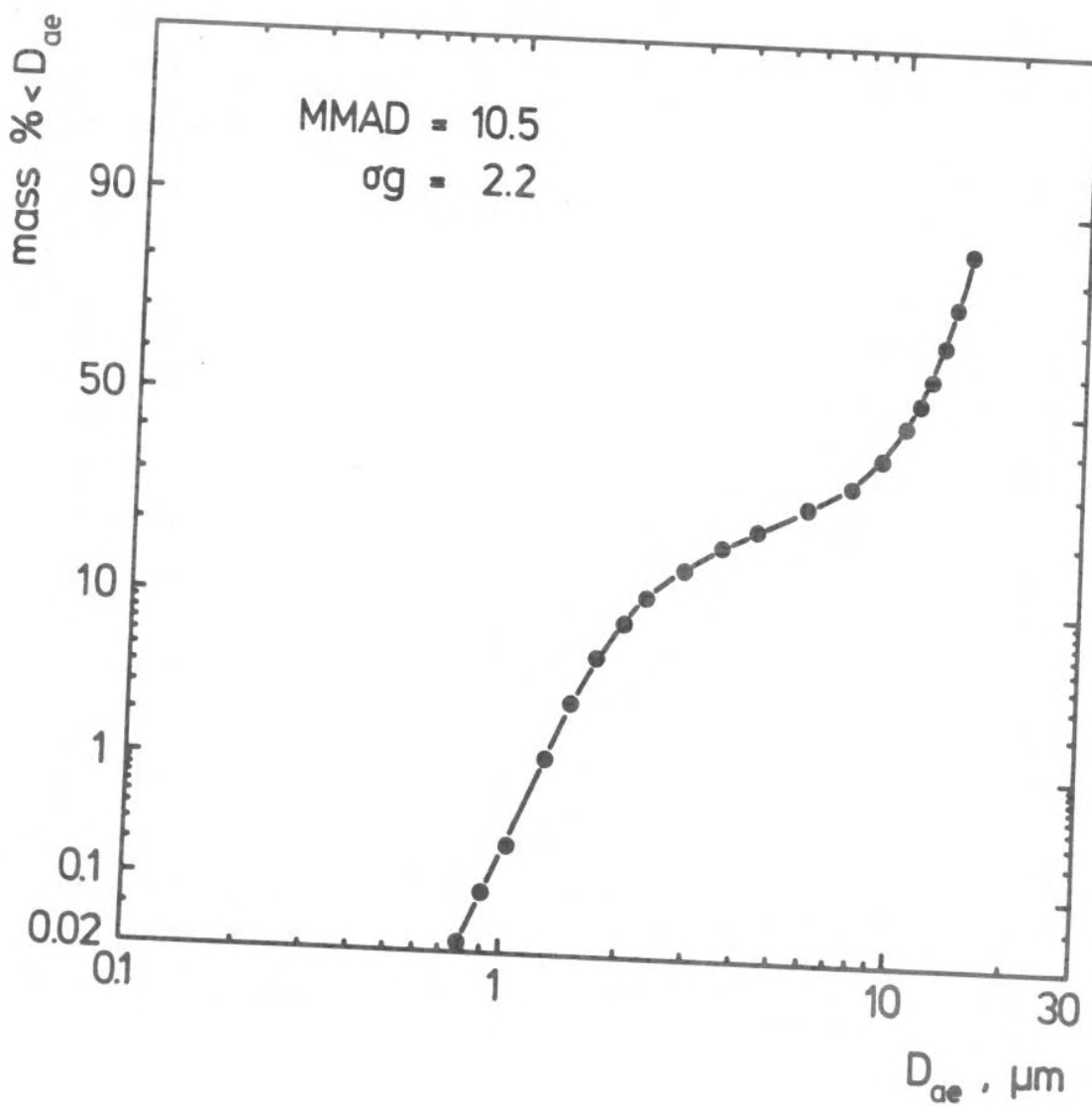


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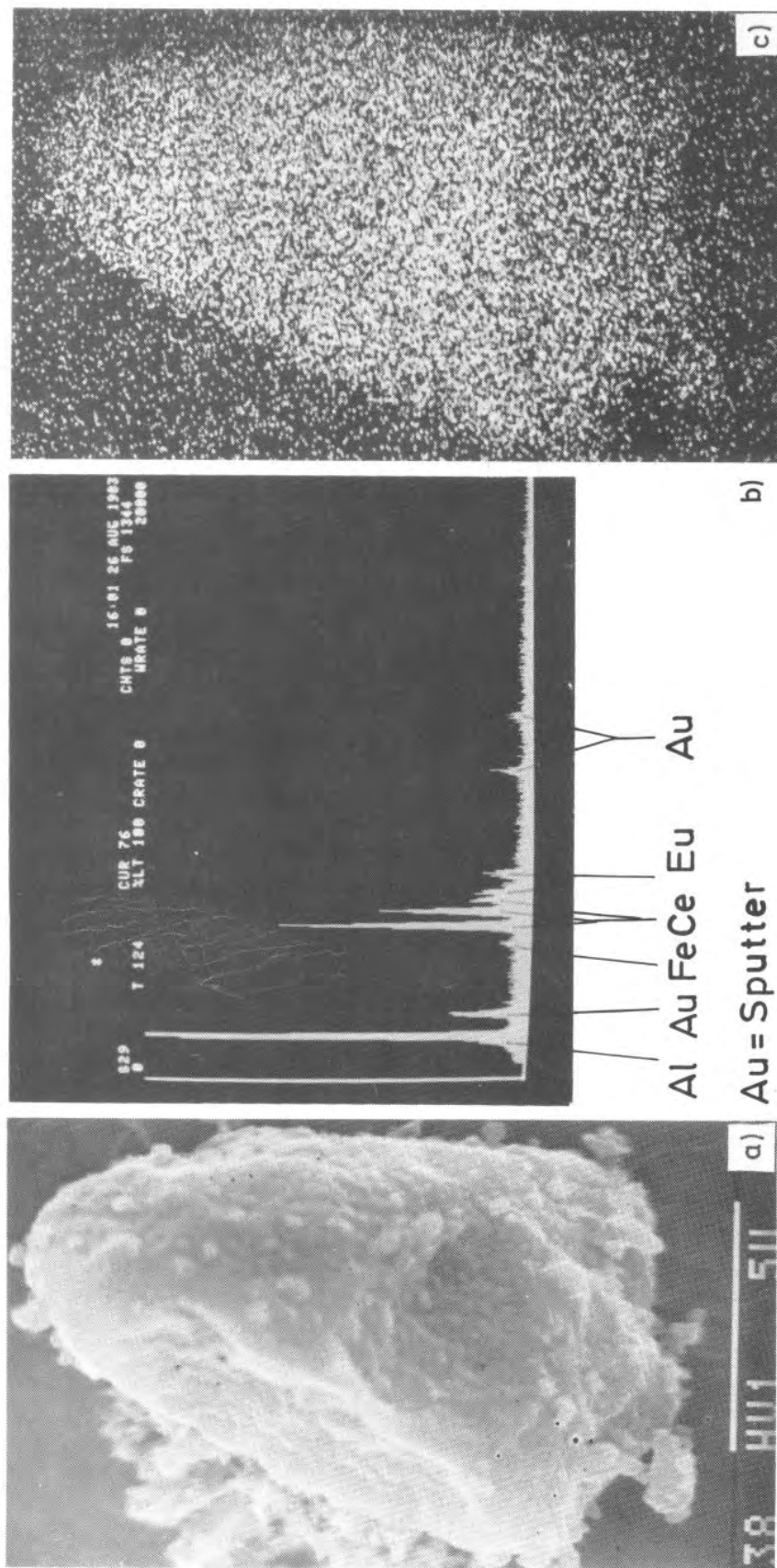


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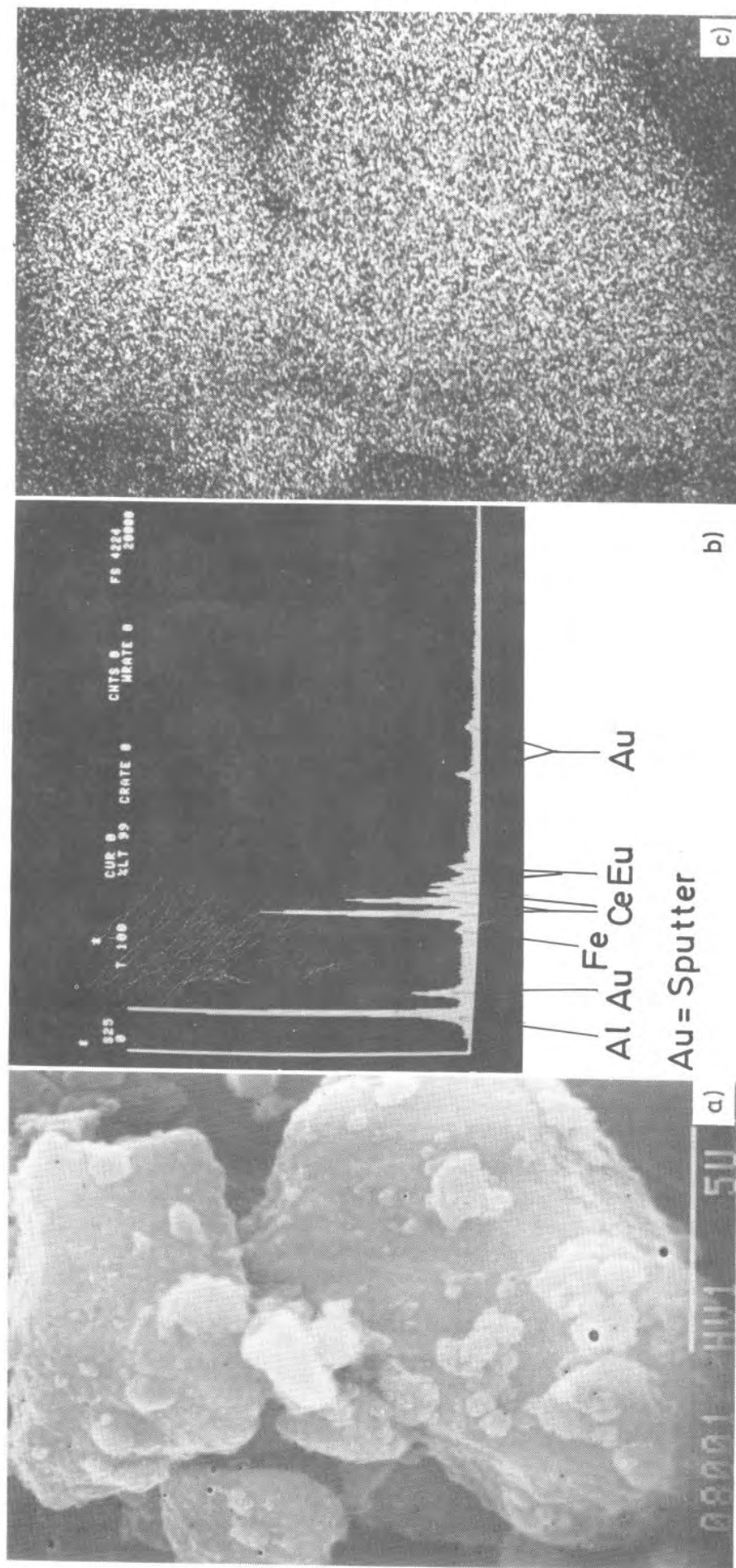


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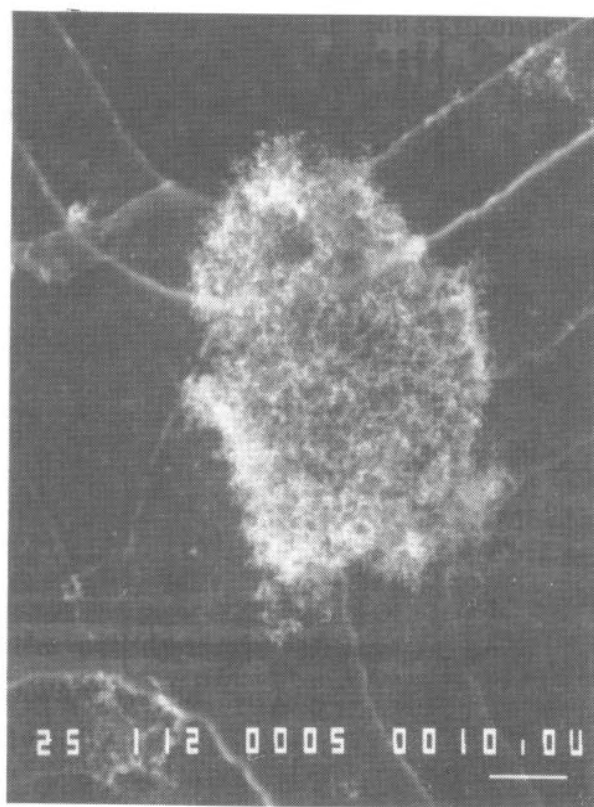


Fig. 12 A soot flake as revealed by scanning electron microscopy



Fig. 13 Transmission micrograph of a particle of extraneous material, together with a mass of soot particles attached to one of the cross pieces of an EM grid

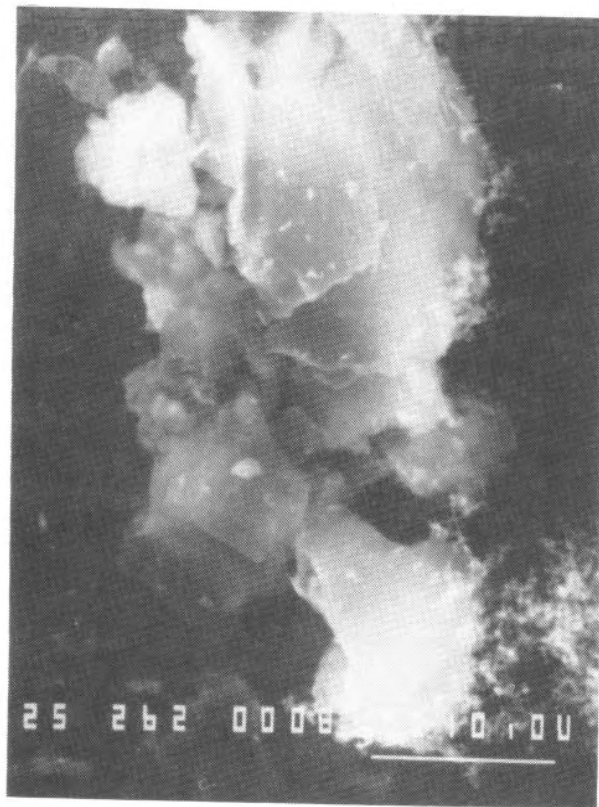


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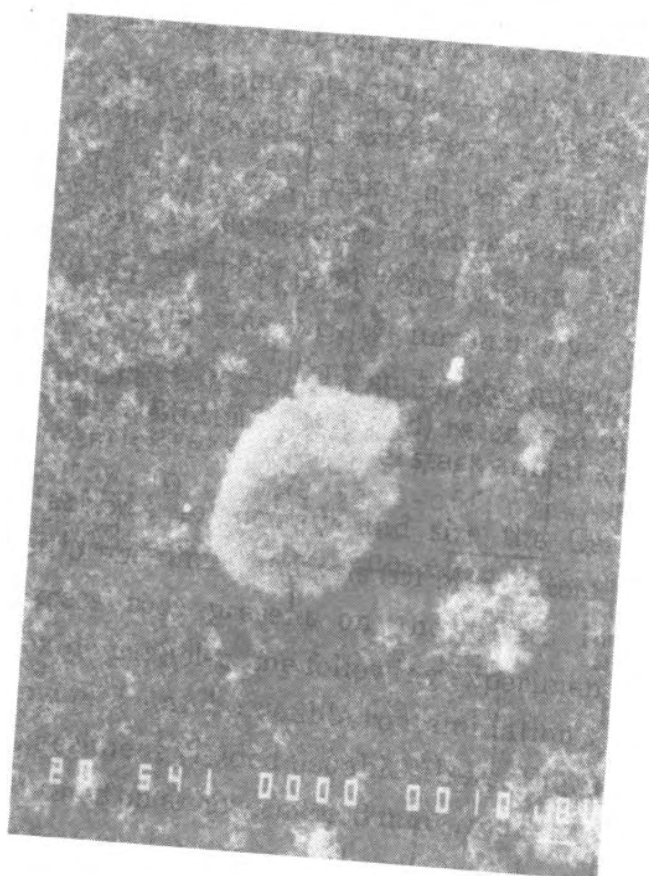


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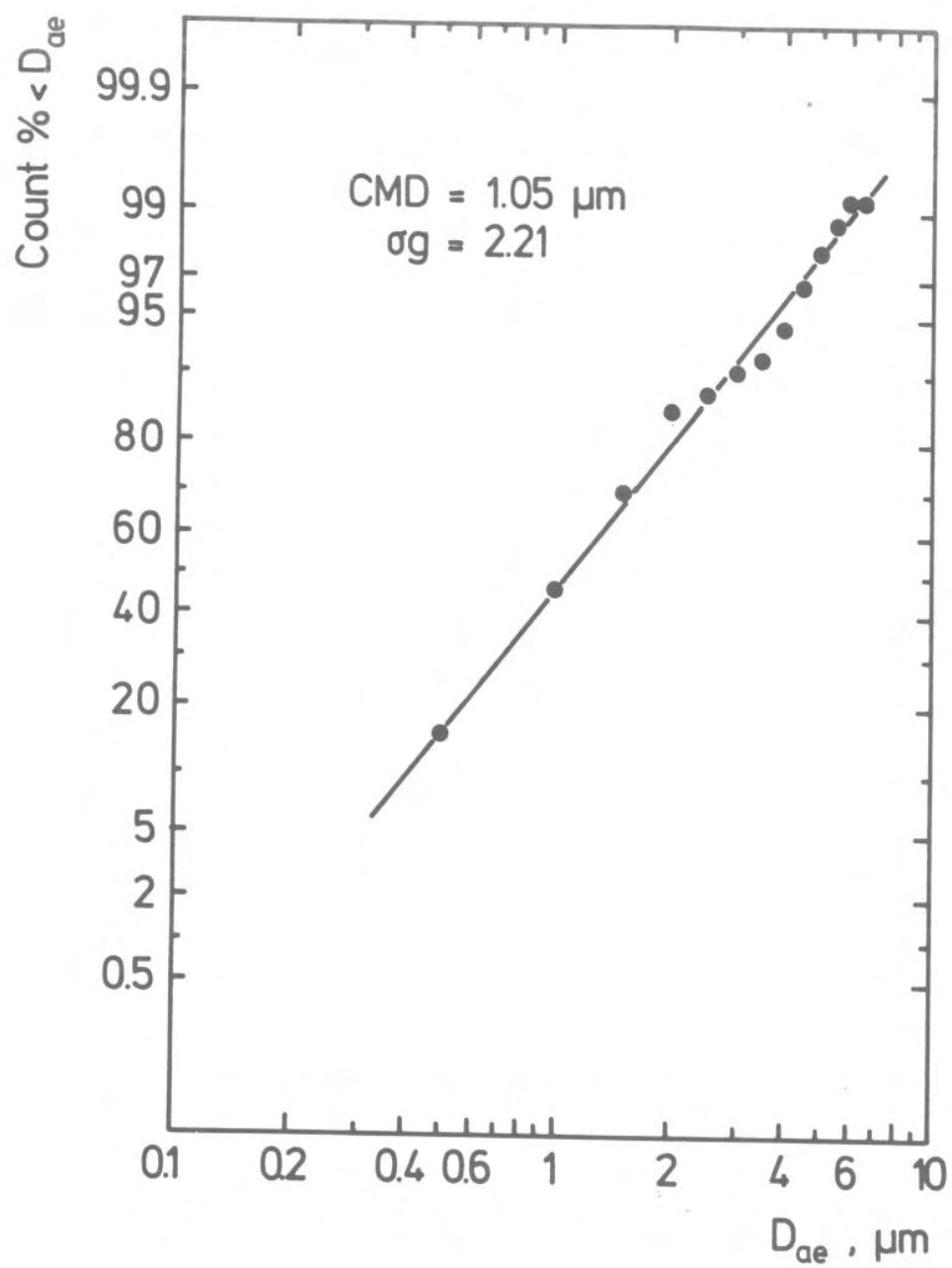


Fig. 16 Size distribution of Ce-Eu-oxide particles; sampling was carried out in the ventilation exit channel 5 min after ignition

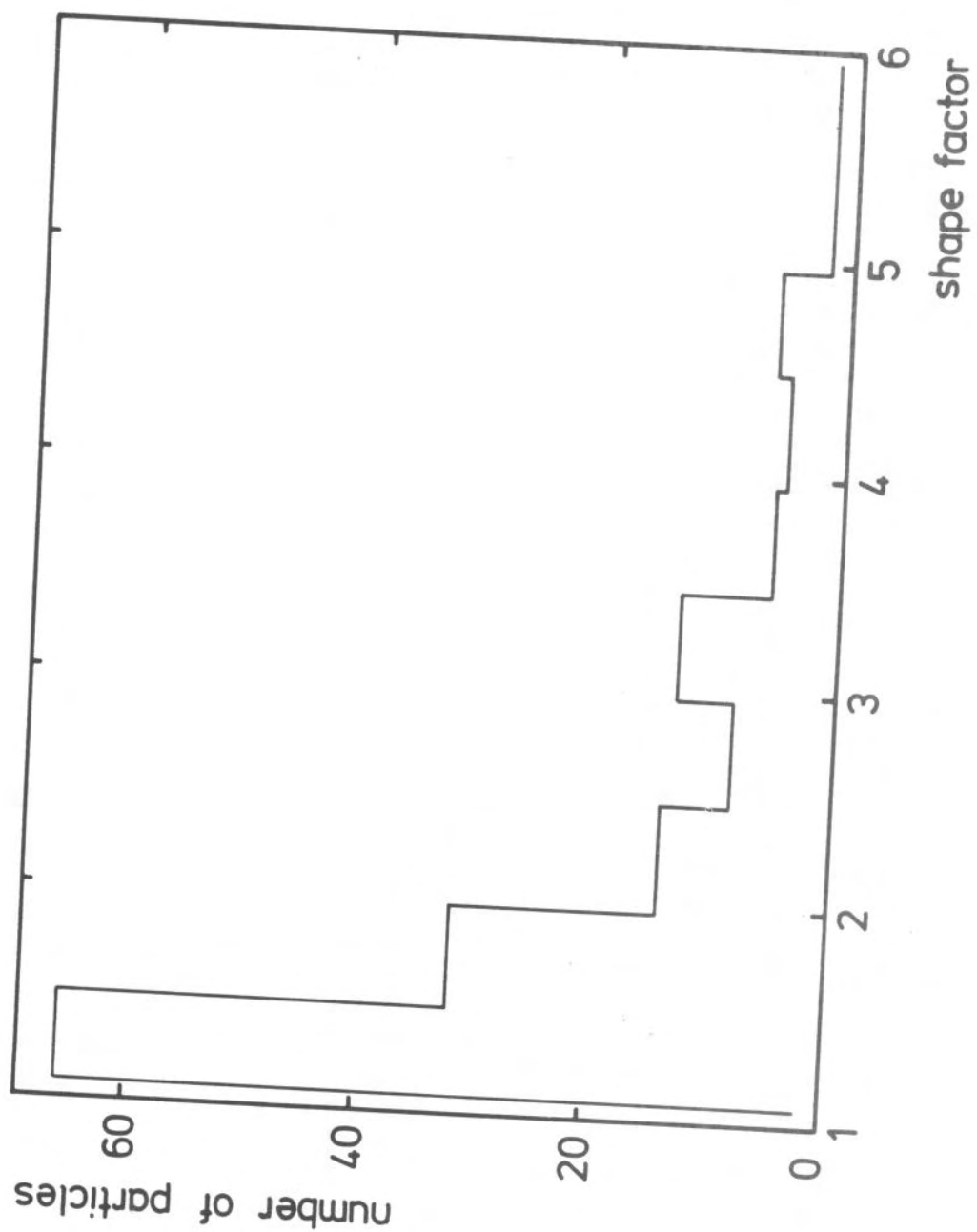


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Experiment Nr. (*)	Rate of ventilation [m ³ h ⁻¹]	M Initial weight of PMMA [kg]	P Maximum Rate of Pyrolysis [g s ⁻¹]	P/M [g s ⁻¹ kg ⁻¹]	Maximum temperature at ceiling [°C]
28	3000	4.9	23.4	4.8	178
29	3000	4.9	23.9	4.9	176
30	2000	4.9	25.0	5.1	208
31	2000	4.9	23.2	4.7	194
32	1000	4.9	22.3	4.6	206
34	450	5.0	21.3	4.3	216
35	500	4.9	24.0	4.9	217
36	3000	1.0	4.5	4.5	53
37	3000	4.9	23.7	4.8	163
38	2000	5.0	21.8	4.4	207
39	1000	4.9	22.3	4.6	218
44	1000	5.0	21.7	4.3	219
45	2000	4.9	21.5	4.4	191
46	2000	4.9	22.3	4.6	200
47	2000	4.9	22.9	4.7	195
48	2000	4.9	23.3	4.8	205
49	2000	4.8	22.7	4.7	209
53	2000	4.9	23.3	4.8	200
54	2000	4.8	22.7	4.7	203
58	2000	4.7	23.8	5.1	220
61	2000	4.9	21.3	4.3	190
62	2000	4.8	22.5	4.7	196
64	2000	4.9	22.0	4.5	201
65	2000	4.8	21.8	4.5	211
66	2000	4.6	21.0	4.6	181
67	2000	4.5	23.3	5.2	196
68	2000	4.6	23.8	5.2	208
70	2000	4.5	21.8	4.8	194
71	2000	4.7	23.9	5.1	216
72	2000	4.9	21.0	4.3	199
76	2000	5.2	23.1	4.4	208
78	2000	5.0	23.6	4.7	200

TABLE 1 Thermal data from a series of test fires

(*) Numbers missing in this list are those of exploratory experiments.

Rate of ventilation [m ³ h ⁻¹]	Mean maximum temperatures [°C]	
	at the ceiling	in the ventilation exit channel
3000	180	85
2000	210	65
1000	220	58
500	230	55

TABLE 2 Some maximum temperatures (mean values) reached in the fire chamber for an initial fuel weight of 4.9 kg of PMMA

Experiment Number	Percent of original contaminant Cerium	
	Transported into the ventilation exit channel	Left in the residues (ashes)
60	1.8	26
65	2.0	27
66	0.5	42
67	1.1	33
68	1.6	43
70	1.4	30
71*	9.8	26
72*	4.2	40
75	1.1	not measured
76	1.5	30
78	1.9	35

TABLE 3 Mass inventory of heavy metal after a contaminated PMMA fire, for a series of standard experiments.

(*) Nr. 71 and 72 had abnormal time patterns, probably due to contamination carry-over.

Experiment Number	Surface concentration of Cerium [mg m ⁻²]												
	a	b	c	d	e	f	g	h	i	j	k	l	m
70	0,70	0,53	0,19	1,32	+	+	+	+	+	+	+	+	+
71	0,61	0,84	0,65	0,41	0,52	0,28	0,49	0,40	0,27	0,15	0,13	0,10	0,07
72	2,84	0,73	0,31	0,23	1,40	0,58	0,58	0,56	0,36	0,09	0,22	0,14	0,09
75	0,97	+	+	+	0,60	0,56	0,37	0,52	0,69	2,22	0,55	0,43	0,19
76	0,93	+	+	+	0,61	0,70	0,87	0,96	1,10	3,19	0,30	0,27	0,16
78	1,12	+	+	+	11,20	0,71	0,43	0,66	1,85	1,71	0,38	0,38	0,25

(+) = not measured

TABLE 4 Heavy metal deposition values at definite locations on the floor (a to i) and on the outer wall at the ventilation outlet side, at a height of 1,50 m (j to m).

Sampling material	Surface concentration of Cerium [mg m ⁻²]			
	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>
Ceramic	0,48	0,49	0,16	0,12
Concrete I	2	1,9	1,1	1,4
Concrete II	0,75	0,32	0,42	0,58
Concrete III	0,46	0,25	0,86	0,34
Aluminium	0,12	0,11	*	0,17

Table 5 Heavy metal deposition values on various sampling plates attached to the ceiling. (The letters (a) to (d) refer to 4 locations, 90° apart around the vertical axis of the fuel stack and at a distance from it of 0,80 m)

* not measured

European Communities — Commission

**EUR 11809 — Contaminated smoke: a simulation of the heavy metal
containing aerosols from fires in plutonium glove boxes**

K. Buijs, B. Chavane de Dalmassy

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For studies of the dispersion of plutonium-bearing aerosols from glove-box fires on a full-size laboratory scale, a special fire-chamber simulating a nuclear fuel handling facility was developed. A 0.6 MW fire source was standardized (reproducibility better than 10%) using PMMA as fuel, to which other glove-box construction materials can be added. Lanthanides were used as substitutes for plutonium for surface contamination of the PMMA. During the fire, 60-75% of the original contaminant becomes airborne, 1-2% is carried away into the ventilation outlet.